1947

The effects of low concentrations of sulphur dioxide on oxidized manganese ores at elevated temperatures

William Henry Magill

Department:

THE EFFECTS OF LOW CONCENTRATIONS OF SULFUR DIOXIDE ON OXIDIZED MANGANESE ORES AT ELEVATED TEMPERATURES

By

WILLIAM HENRY MAGILL

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1947

Approved by W T Schrenk

Chairman, Department of Chemical Engineering and Chemistry

TABLE OF CONTENTS

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. W. T. Schrenk, Chairman of the Department of Chemical Engineering and Chemistry, Missouri School of Mines and Metallurgy, for his guidance and suggestions throughout this investigation and the preparation of this thesis.

TABLES

FIGURES

INTRODUCTION

Manganese is a metal of strategic importance. Each net ton of steel requires approximately 12.5 pounds of manganese, and this, with its many other uses, requires well over a million tons of 50 per cent ore in one year. Normally the United States imports about 96 per cent of its requirements from Russia, South America, and South Africa(1), but during a national crisis, such as that just past, this would be impossible. Under such conditions the Nation would be dependent to a great extent upon domestic sources for ore.

Although there are large quantities of manganese ore(2) in the United States, most of it is low-grade and cannot be used for the production of ferromanganese. Much government and private research has been done to concentrate the domestic low-grade ores but many problems have been encountered. A large number of treatments have been found necessary for ores from various sections of the country.

Low-grade ores have been sulfated with sulfur dioxide in the gaseous state at elevated temperatures and the soluble manganous sulfate extracted with water(3). This gave a solu-

---

(1) U. S. Bureau of Mines. Minerals Yearbook, 1940. Manganese and manganiferous ores. p. 583.

(2) Dean, R.S., and others; Manganese: Its Occurence, Milling, and Metallurgy: U. S. Bureau of Mines. Information Circular 6770, 1934.

(3) Pietz, E. Recovery of manganese from oxidized ores as iron-and phosphorous-free soluble salts. Thesis, Missouri School of Mines, Rolla, Mo.

tion of manganous sulfate that may be used for the recovery of manganese by many available methods. It was believed that with proper conditions of temperature, concentration of sulfur dioxide, and other variables, it would be possible to use a non-commercial supply of sulfur dioxide and obtain a soluble manganese salt of commercial significance.

These factors led to the selection of this subject as a research problem.

REVIEW OF PREVIOUS WORK

During the last two periods of war this country has found its supply of high-grade manganese ores practically cut off. Normally there are enough high-grade ores available from other countries that it is not profitable for the iron and steel industry to spend time and money to concentrate the low-grade domestic supplies. The imported ores are concentrated enough so they may be used directly in the production of steel. The process is essentially a reduction with carbon in a blast furnace to produce ferromanganese, a manganese-iron alloy. The more siliceous ores are treated in the blast furnace to produce spiegeleisen, an alloy of iron-silicon-manganese.

Beginning in 1914, and all during the first world war, several processes were developed for the recovery of manganese from low-grade ores. A number of large deposits(4) of low-grade ore were found in this country which warranted investigation. Following the war, when the high-grade ores were again available, these processes were discontinued. In recent years this investigation has received even greater interest than before.

In this revival of investigation the hydrometallurgical treatment of ores for producing a high-grade manganese concentrate has probably received more attention than any other

---

(4) Dean, R.S., Leaver, E.S., and Joseph, T.L. Manganese. U. S. Bureau of Mines. Information Circular 6770. 1934. pp. 168-9

type of process. The treatment of low-grade manganese ores by this type of process presented some difficult problems in comparison with the usual leaching processes used in recovering the precious metals or copper. In the extraction of manganese by such methods, the solvent must be cheap or must lend itself to regeneration for repeated use in the process at low cost. Another problem was the recovery of the manganese from the leaching solution. The cost of such treatment and the selling price of the product governed the feasibility of employing the process.

"From a hydrometallurgical standpoint manganese ores may be divided into several types: (1) Ores in which the manganese mineral is readily soluble in at least one solvent; (2) ores in which the manganese requires preliminary treatment to make it soluble; (3) ores containing manganese in insoluble form; (4) ores which destroy excessive amounts of solvents due to soluble impurities; (5) ores which present physical properties that increase the cost of treatment."(5)

Pyrolusite, braunite, and the other higher oxides will be included in group (1). Since rhodochrosite requires a preliminary roast to expell the carbon dioxide, it will be classified in group (2). Group (3) is made up of such ores as rhodonite and the partially oxidized black silicate. Ores having a high lime content, causing excessive acid consumption, represent group (4). Group (5) is made up of ores con-

---

(5) Ibid. p. 167.

taining clay and talc.

The Leaver drum-leaching process[6], for which E. S. Leaver received a patent in 1918[7], was one of the first important processes developed for treating domestic low-grade manganese ores. In this process hot smelter gases containing from 2 to 6 per cent sulfur dioxide were passed countercurrent to a pulp of 20-mesh ore in water. The higher oxides of manganese were found to be readily dissolved in the hot sulfurous acid solution. The manganese was recovered from the solution by evaporation followed by sintering. The evaporation regenerated the sulfur dioxide which could be used again in the process.

Two processes[8] for sulfating manganese ores were developed by Professor A. T. Sweet and his associates at the Michigan School of Mines. One of these processes was called the "Sweet ammonia process" and the other was called the "Sweet acid process".

For the ammonia process the ore was crushed to minus 65-mesh, mixed with ammonium sulfate and moistened. This pulp was roasted to drive off the carbon dioxide and ammonia. These gases were passed into water forming an ammonium carbonate solution which was used later to precipitate the man-

---

(6) Ibid. p. 180-3.

(7) Leaver, E.S., Leaver drum-leaching process. U. S. Pat. 243,015, Nov. 18, 1918.

(8) Dean, R.S., Leaver, E.S., and Joseph, T.L. Manganese. U. S. Bureau of Mines. Information Circular 6770. 1934. p. 177.

ganese. The roasted pulp was leached with water in a counter-current system. The manganese was then removed from the clarified leach solution by precipitating it with ammonium carbonate solution. This step regenerated the ammonium sulfate. The manganous carbonate was filtered off and converted to a manganese sinter. This process is especially applicable to ores high in carbonates.

In the acid process the ore was crushed to 65-mesh, mixed with sulfuric acid and roasted in a Herreshoff roasting furnace with a maximum temperature of 790°C. The roasted ore was leached with water and the solution filtered. The filtrate was evaporated to precipitate the manganous sulfate which was converted to the high temperature oxides of manganese by sintering. The acid process is applicable to ores low in lime and magnesia.

The Bradley process(9) was another important process. In this process the ore was crushed to minus 65-mesh and roasted at 400°C in a reducing atmosphere of producer or blast furnace gas. This treatment converted the manganous dioxide to manganous oxide and the ferric oxide to the magnetic oxide and a small amount of ferrous oxide according to the following equations:

$$MnO_2 + CO = MnO + CO_2$$

$$3Fe_2O_3 + CO = 3Fe_3O_4 + CO_2$$

---

(9) Zapffe, Carl. Leaching manganese from the siliceous iron ores of Minnesota. Eng. Mining J. Vol. 127, pp. 1039 and Vol. 128, pp. 14-9 (1929).

$$Fe_3O_4 + CO = 3FeO + CO_2$$

The manganese was extracted from the reduced ore by leaching with ammonium sulfate solution. This dissolved the manganous and ferrous oxides and liberated ammonia. The pulp was filtered and the ammonia passed into the filtrate to precipitate manganous hydroxide and regenerate ammonium sulfate. Air was next passed through the solution to convert the manganous hydroxide to the partially dehydrated manganic hydroxide according to the following equation:(10)

$$2Mn(OH)_2 + O = 2MnO \cdot OH + H_2O$$

The precipitate was filtered off, dried, and converted to the high-temperature oxides by sintering, thus producing a product satisfactory for the production of ferromanganese.

During the recent war years the U. S. Bureau of Mines did a great deal of research in producing ferromanganese from domestic low-grade ores. Most of the reports of investigations have been restricted and some of the work involving sulfating with sulfur dioxide has not been published as yet. The investigations included laboratory studies concerned with ore dressing, hydrometallurgy, electrometallurgy, and pyrometallurgy. Pilots plants have been constructed for the purpose of intensive study of various phases of the manganese metallurgy.

The U. S. Bureau of Mines has made a study of a large

---

(10) Dean, R.S., Leaver, E.S., and Joseph, T.L. Manganese. U. S. Bureau of Mines. Information Circular 6770. 1934. p. 177.

number of ores from an ore dressing standpoint. In their investigations they found that approximately four out of five may be concentrated to ferro-grade with an average recovery of 75 per cent of the manganese in the ore. The difficulty encountered in this investigation was the fact that each ore was found to present a distinct ore dressing problem. The methods of ore dressing employed by the Bureau of Mines are(11): Log washing and rejecting the clays and slimes; attrition grinding; jigging; "sink and float", employing an aqueous suspension of finely divided galena; tabling in closed circuit with grinding; tabling classified and unclassified feeds; flotation of manganese minerals; flotation of calvite, fluorite, and gypsum; flotation of siliceous material by use of cationic reagents; table agglomeration; slime treatment; and magnetic separation. In most cases a combination of several of these methods was employed in concentrating the ore. The recoveries of manganese ranged from 20 to 95 per cent of that present in the ore.

There have been ores found that are not amenable either to concentration by ore dressing or hydrometallurgical processes. These ores may be smelted with iron or copper sulfides to a manganese matte and refined to a 60 per cent manganese product that meets ferro-grade specifications(12). The type

---

(11) Dean, R.S. Progress Reports-Metallurgical Division. U. S. Bureau of Mines. Report of Investigations 3600. 1941. pp. 10-3.

(12) Ibid. pp. 15-9.

of manganese ore best suited to matte-smelting are those which contain twice as much silica as lime plus magnesia.

There were a large number of hydrometallurgical processes proposed but only those that were promising and well known and a few that appeared applicable were studied intensively. Low-grade domestic ores that were not amenable to concentration were studied from the hydrometallurgical standpoint(13).

A study has been made of the optimum conditions for the sulfating of low-grade domestic manganese ores with gaseous sulfur dioxide(14). In this study the effects of temperature on sulfating were found and also the effects of sulfur dioxide concentration were investigated to some extent. The ore was placed in a high temperature tube furnace and the sulfur dioxide gas passed over it. The treated ore was then leached with water to extract the soluble manganese sulfate. The treatment of various types of ores gave recoveries of from 7 to 80 per cent of the manganese present in the ore.

---

(13) Ibid. pp. 20-3

(14) Pietz, Emil. Recovery of manganese from oxidized ores as iron-and phosphorous-free soluble salts. Thesis, Missouri School of Mines, Rolla, Mo.

EQUIPMENT

All the experiments in this study were performed in a two-tube Burrell high-temperature furnace. This furnace was equipped with a thermocouple attached to a calibrated temperature indicator.

REAGENTS

Potassium Permanganate Solution

This solution was prepared in carboy lots by dissolving enough reagent grade potassium permanganate in distilled water to make a solution of approximately 0.1 N strength. This solution was allowed to age to insure a more constant strength. Weighed samples of 0.2 grams of standard sodium oxalate dissolved in 75 ml of 1:20 sulfuric acid at 65° C were titrated with the permanganate solution in the standardization.

Ammonium Sulfate Solution

This was a water solution containing 100 grams of ammonium sulfate per liter.

Sulfur Dioxide

In all of this work this gas was obtained from a cylinder of liquid sulfur dioxide.

SAMPLES

The samples used in this research came from deposits of low-grade manganese ores in the Batesville district, near Batesville, Arkansas. The samples were all ground to minus 100-mesh. These are the same samples used by Pietz[15] in his study of sulfating oxidized ores with sulfur dioxide. The analyses for these five Arkansas wad ores are given in Table I.

Table I. Analyses of the Arkansas Wad Ores.

Ore	Mn	Fe	CaO	SiO_2	P	Insol.
Ark 1	23.55	20.96	7.62	7.34	2.42	10.56
Ark 2	31.90	24.18	----	3.40	0.22	5.92
Ark 3	29.77	21.82	0.56	6.64	0.61	11.62
Ark 4	31.60	14.00	5.79	9.32	1.68	13.68
Ark 5	27.00	23.93	4.11	7.04	1.45	9.56

(15) Ibid.

PROCEDURE

Determination of Manganese

The manganese in each leaching was determined by the Volhard[16] method. Two ml of sulfuric acid (sp. g. 1.84) and 10 grams of zinc sulfate were added to the leach solution. After the zinc sulfate was dissolved an emulsion of zinc oxide in water was added in excess to neutralize the acid and precipitate any iron and aluminum that may have been extracted. The solution was diluted to 500 ml. Aliquot portions of this solution were heated to boiling and titrated hot with a standard potassium permanganate solution.

---

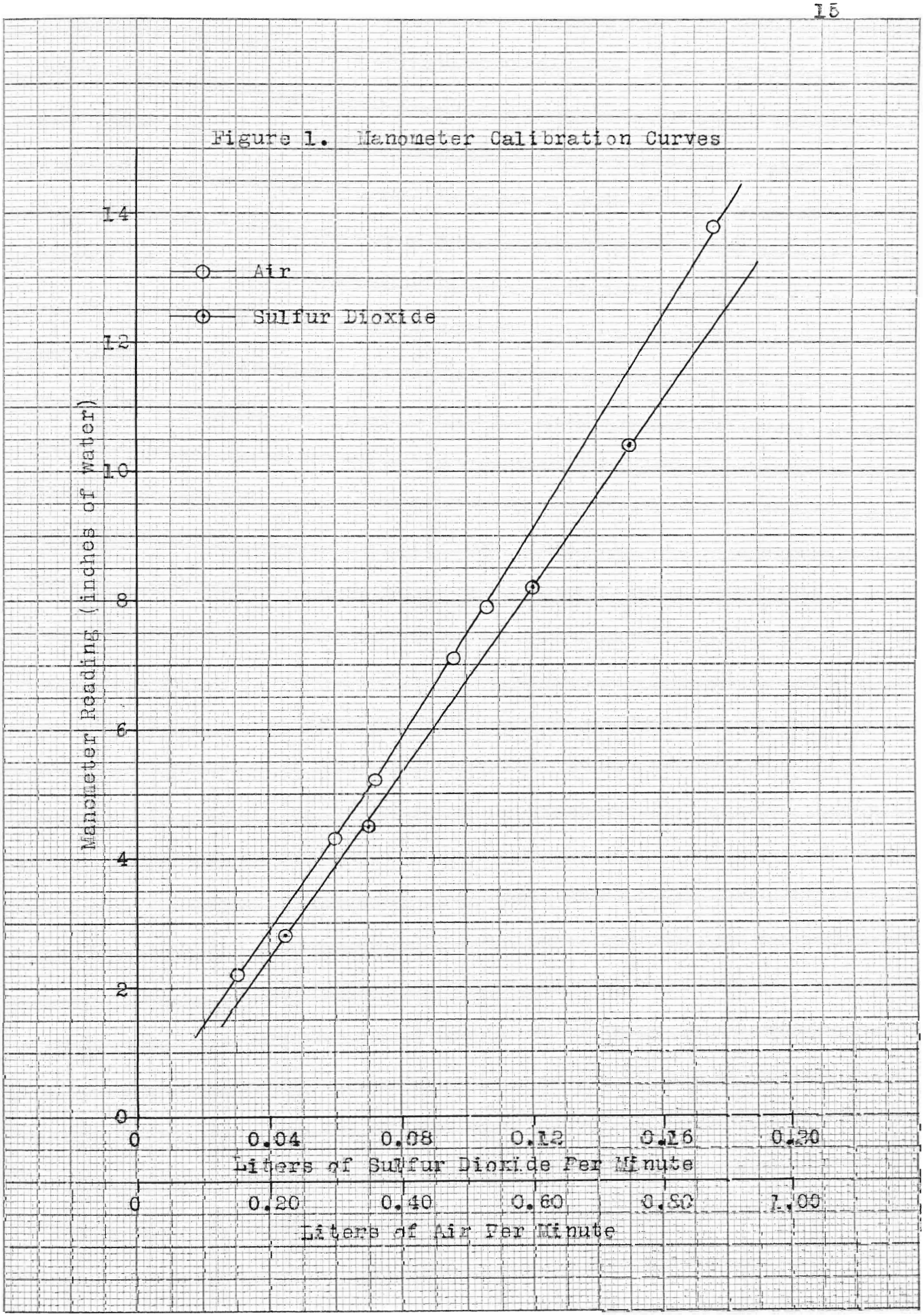
(16) Lord, N.W. and Demorest, D.J. Metallurgical Analysis. 5th ed. N.Y., McGraw-Hill, 1924. pp. 81-4.

CALIBRATION OF FLOW-RATE APPARATUS

A cylinder of liquid sulfur dioxide was used in these experiments to make it possible to control the rate at which the gas was used. The compressed air produced at the power plant was used. The two gases were mixed by passing them into a Woulff bottle, then through a tube packed with glass wool and then to the furnace.

A capillary tube was placed in each line as an orifice. The back pressure was measured in each line by the use of a water manometer. Each capillary tube was calibrated by passing air through at different rates and measuring the time taken to displace a measured volume of water. The rate, in liters of gas at room temperature per minute, was plotted against the pressure, in inches of water, to obtain the curves in Figure I. The rate of flow was very small and, therefore, neither circuit caused a back pressure in the other.

Figure 1. Manometer Calibration Curves



PRELIMINARY EXPERIMENTS

For preliminary experiments in this study a number of runs were made under the same conditions used by Pietz[17] in an effort to duplicate his results. He found that the optimum temperature for sulfating oxidized ores with sulfur dioxide was 650° C. He also found that, for the size of sample used and for the apparatus used, the reaction was nearly complete in 15 minutes. A time of 45 minutes was used for all his remaining experiments. This insured a fairly complete reaction because it would tend to offset variations in the treatment that could not be controlled. According to other data collected by Pietz, a concentration of sulfur dioxide of 40 per cent gave the best recovery.

Weighed samples of the manganese ores were placed in combustion boats which in turn were placed in the two-tube combustion furnace at 650° C. A mixture of dry sulfur dioxide and air was passed through the furnace for an interval of 45 minutes. This mixture consisted of 40 per cent sulfur dioxide and 60 per cent air. The cooled samples were leached with water and the soluble manganese in each leaching was determined.

The results of these experiments are shown in Table II.

---

(17) Ibid.

Table II. Preliminary Experiments
(SO_2 rate - 0.154 liter per minute)
(SO_2 concentration - 40 per cent by volume)
(Temperature - 650°C; Time - 45 minutes)

Exp. No.	Ore	Per cent of total Mn recovered	Pietz's recovery
1	Ark 1	53.82	53.70
2	Ark 2	63.50	63.48
3	Ark 3	51.00	51.74
4	Ark 4	32.95	33.20
5	Ark 5	35.54	35.60

The temperature of 650° C used in these experiments is above the decomposition temperature[18] of ferrous sulfate (480°C) and, therefore, no iron should be extracted with water. Pietz found that above 700° C the amount of extraction of manganese drops off rapidly. This is due to the fact that manganous sulfate begins to decompose at 699° C[18].

Dense white fumes of sulfur trioxide were noticed leaving the gas exhaust during these experiments. This was probably caused by the catalytic oxidation of the sulfur dioxide according to the following equation:

$$2SO_2 + O_2 \text{ — } 2SO_3$$

---

(18) Hodgman, C.D., and Holmes, H.N. Handbook of Chemistry and Physics. 25th ed. Cleveland, Chemical Rubber Publishing Co., 1941. p. 1449.

EFFECT OF MOIST GAS ON EXTRACTION

A series of experiments were run to study the effect of a slight amount of moisture in the gas on the percentage extraction. The air was bubbled through a flask of water at room temperature before mixing with the sulfur dioxide. By knowing the vapor pressure of water at that particular temperature the per cent of water vapor by volume in the air could be calculated. At ordinary room temperature this gave about 1.8 per cent of water vapor in the air.

Samples of the five Arkansas ores were treated with this mixture of moist gases at 650° C for 45 minutes. The rates of sulfur dioxide and air remained the same as in the preliminary experiments. This gave a mixture of 40 per cent sulfur dioxide, 58.9 per cent air, and 1.1 per cent water vapor. The cooled samples were leached with water and the soluble manganese determined.

Table III shows the effect of this small amount of moisture on the percentage extraction. In general it can be seen that the 1.1 per cent of water vapor increased the recovery about 10 per cent.

Table III. Effect of Moist Gas on Extraction
(SO_2 rate - 0.154 liter per minute)
(SO_2 concentration - 40 per cent by volume)
(H_2O vapor concentration - 1.1 per cent by volume)
(Temperature - 650°C; Time - 45 minutes)

Exp. No.	Ore	Per cent of total Mn recovered
1	Ark 1	63.20
2	Ark 2	77.52
3	Ark 3	63.31
4	Ark 4	43.51
5	Ark 5	48.42

SULFATING WITH MOIST, DILUTE SULFUR DIOXIDE

In this series of experiments all conditions were maintained the same as in the previous runs made with moist gases except that the sulfur dioxide was diluted with air to a concentration of only 5 per cent. The air was bubbled through water at room temperature. This gave a gas mixture of 5 per cent sulfur dioxide, 93.3 per cent air, and 1.7 per cent water vapor. Weighed samples of the five Arkansas ores were placed in combustion boats and treated with this mixture in the Burrell furnace for 45 minutes at 650° C. The cooled samples were leached with water and the soluble manganese determined.

Table IV shows the results of these experiments. In every case but one the recovery in these experiments was higher than in those where dry 40 per cent sulfur dioxide was used.

Table IV. Sulfating With Moist, Dilute Sulfur Dioxide
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(H_2O vapor concentration - 1.7 per cent by volume)
(Temperature - 650°C; Time - 45 minutes)

Exp. No.	Ore	Per cent of total Mn recovered
1	Ark 1	54.76
2	Ark 2	62.10
3	Ark 3	54.21
4	Ark 4	38.67
5	Ark 5	42.35

To study further the effects of moisture on the percentage recovery of manganese another series of experiments was run using different amounts of moisture in the gas mixture. The amount of moisture was controlled in the same manner as before. The air was bubbled through water at four different temperatures which gave four concentrations of water vapor in the gas mixture due to the change in vapor pressure of the water.

Samples of the Arkansas (1) ore were treated with these mixtures of moist gases at 650° C for 45 minutes with constant rates of sulfur dioxide and air. The cooled samples were leached with water and the soluble manganese determined. The results of these experiments are shown in Table V.

Pietz[19] made a series of studies on the effect of moisture on percentage extraction and found that maximum extraction was obtained with gases containing from 25 to 30 per cent (by volume) moisture. He controlled the amount of moisture by adding water from a burette through a capillary tube to a heated portion of the furnace tube. This caused the water to vaporize and mix with the entering air and sulfur dioxide. The percentage composition of the gases was calculated, assuming that all the water added was vaporized and passed through the furnace.

---

(19) Pietz, Emil. Recovery of manganese from oxidized ores as iron-and phosphorous-free soluble salts. Thesis, Missouri School of Mines, Rolla, Mo.

Table V. Sulfating With Moist, Dilute Sulfur Dioxide
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(Temperature - 650°C; Time - 45 minutes)

Exp. No.	Ore	Water temp. °C	Gas composition (per cent by vol)			Per cent of total Mn recovered
			Air	SO_2	H_2O	
1	Ark 1	20	93.3	5	1.7	54.76
2	"	40	87.8	5	7.2	55.72
3	"	50	85.3	5	9.7	56.96
4	"	60	81.3	5	13.7	59.00

EFFECTS OF VARIABLE TEMPERATURE

In this series of experiments the ore was placed in the cold furnace and sulfur dioxide was passed over it while the furnace was heated up to 650° C. This took approximately 1 hour and 30 minutes. After the furnace reached the optimum temperature it was held there for 15 minutes with the gas mixture still passing through it. The gas mixture consisted of 5 per cent sulfur dioxide, 93.3 per cent air, and 1.7 per cent water vapor. Two gram samples of the five Arkansas wad ores were treated in these experiments. After the samples were cooled they were leached with water and the soluble manganese determined.

The insoluble residues from the above runs were leached with an ammonium sulfate solution (100 g. $(NH_4)_2SO_4$ per liter). The additional manganese extracted was considered to have been in the form of manganous oxide.

$$MnO + (NH_4)_2SO_4 \text{ — } MnSO_4 + 2NH_3 + H_2O$$

The presence of the manganous oxide may have been due to some local overheating in the ore.

$$MnSO_4 \text{ — } MnO + SO_3$$

The results of these experiments are shown in Table VI.

Table VI. Effects of Variable Temperature
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(H_2O vapor concentration - 1.7 per cent by volume)

Exp. No.	Ore	Water leaching per cent of total Mn	$(NH_4)_2SO_4$ leaching of residue per cent of total Mn
1	Ark 1	57.84	3.70
2	Ark 2	65.31	3.43
3	Ark 3	57.14	3.01
4	Ark 4	40.44	2.77
5	Ark 5	45.06	2.96

It was believed that some increase over previous recoveries might be obtained if the ore was also treated while it was cooling. Samples of the five Arkansas ores were placed in the cold furnace and treated with 5 per cent sulfur dioxide containing 1.7 per cent water vapor while the furnace was heated up to 650° C. This required 1 hour and 30 minutes. The ores were treated for 15 minutes at 650° C and for 1 hour while they were cooling. The cooled samples were leached with water and the soluble manganese determined. Table VII shows that this treatment gave a small increase over the experiments shown in Table VI.

Table VII. Effects of Variable Temperature
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(H_2O vapor concentration - 1.7 per cent by volume)

Exp. No.	Ore	Per cent of total Mn recovered
1	Ark 1	61.42
2	Ark 2	70.15
3	Ark 3	60.86
4	Ark 4	44.32
5	Ark 5	49.70

EFFECTS OF MOISTENING ORE WITH SULFURIC ACID

A 2 gram sample of Arkansas ore number (1) was moistened with 2 ml of water and treated in the Burrell furnace with 5 per cent sulfur dioxide. To prevent the ore from sputtering out of the combustion boat due to the water present, the ore was placed in the cold furnace and treated with sulfur dioxide while the furnace was heated up to 650° C. This required 1 hour and 30 minutes. The ore was treated for an additional 15 minutes at 650° C. The sample was leached with water and the soluble manganese determined. This particular experiment gave no noticeable increase over previous runs in percentage recovery.

It was thought that some increase might be obtained if the ore was moistened with sulfuric acid. A sample of ore number (1) was moistened with 2 ml of concentrated sulfuric acid (sp. g. 1.84) and treated in the furnace as above. The cooled sample was leached with water and the soluble manganese determined. This increased the recovery to 73.85 per cent which is about 20 per cent above previous recoveries. As a result of this experiment the other four Arkansas ores were treated.

1 ml of 6N sulfuric acid contains enough sulfuric acid to react with 2 grams of manganese dioxide. The five ores were moistened with this amount of acid and also with 50 per cent and 5 per cent of this amount. Each sample was treated with 5 per cent sulfur dioxide. Tables VIII, IX, and X present the results of these experiments.

Table VIII. Effects of Moistening Ore With Sulfuric Acid
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(H_2O vapor concentration - 1.7 per cent by volume)

Exp. No.	Ore	Amount of H_2SO_4	Per cent of total Mn recovered
1	Ark 1	2 ml 3N	68.52
2	Ark 2	" "	72.14
3	Ark 3	" "	67.94
4	Ark 4	" "	59.65
5	Ark 5	" "	63.47

Table IX. Effects of Moistening Ore With Sulfuric Acid
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(H_2O vapor concentration - 1.7 per cent by volume)

Exp. No.	Ore	Amount of H_2SO_4	Per cent of total Mn recovered
1	Ark 1	2 ml 1.5N	66.48
2	Ark 2	" "	71.30
3	Ark 3	" "	66.00
4	Ark 4	" "	58.75
5	Ark 5	" "	61.52

Table X. Effects of Moistening Ore With Sulfuric Acid
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(H_2O vapor concentration - 1.7 per cent by volume)

Exp. No.	Ore	Amount of H_2SO_4	Per cent of total Mn recovered
1	Ark 1	2 ml 0.15N	65.93
2	Ark 2	" "	70.78
3	Ark 3	" "	64.86
4	Ark 4	" "	57.15
5	Ark 5	" "	60.52

The insoluble residues from the runs shown in Tables VIII, IX, and X were leached with ammonium sulfate (100 g. $(NH_4)_2SO_4$ per liter). These leachings showed that there was no additional manganese present that was extractable with ammonium sulfate.

Commercially, it would not be practical to moisten the ores with concentrated sulfuric acid to increase the recovery of the manganese. These experiments show, however, that very dilute solutions of sulfuric acid gave practically the same percentage recovery as did the 6N solutions.

EFFECTS OF LEACHING WITH SULFURIC ACID

After finding the effects of moistening the ore with sulfuric acid, a series of experiments was run to find the effects of leaching the treated ores with sulfuric acid. The five Arkansas ores were treated in the Burrell furnace for 45 minutes at 650° C with a 5 per cent sulfur dioxide gas mixture. This mixture contained 1.7 per cent water vapor. The cooled samples were leached with 1:20 sulfuric acid and the soluble manganese determined. The results of these experiments are shown in Table XI.

Table XI. Effects of Leaching With Sulfuric Acid
(SO_2 rate - 0.042 liter per minute)
(SO_2 concentration - 5 per cent by volume)
(H_2O vapor concentration - 1.7 per cent by volume)
(Leached with 1:20 sulfuric acid)

Exp. No.	Ore	Per cent of total Mn recovered
1	Ark 1	68.45
2	Ark 2	81.20
3	Ark 3	68.25
4	Ark 4	58.53
5	Ark 5	61.52

A comparison of the extractions of manganese with sulfuric acid and ammonium sulfate (Table VI) indicated that only a small amount of manganous oxide was present and extracted with ammonium sulfate. The reduction of a portion of the manganous sulfate due to local overheating of the ore has previously been shown as an explanation of the presence of manganous oxide. A greater amount was present as the sulfite as indicated by the extraction with acid. The sulfite was probably produced by a direct combination of the monoxide and sulfur dioxide, represented by the equation:

$$MnO + SO_2 \text{ — } MnSO_3$$

The reactions involved in the extraction with sulfuric acid are probably the following:

$$MnSO_3 + H_2SO_4 \text{ — } MnSO_4 + H_2O + SO_2$$

$$MnO + H_2SO_4 \text{ — } MnSO_4 + H_2O$$

RELATION BETWEEN AMOUNT OF MANGANESE AS THE DIOXIDE AND PERCENTAGE EXTRACTION

It was believed that the amount of extraction in the experiments in this study was directly effected by the percentage of the manganese in the ore as manganese dioxide. To evaluate this percentage the available oxygen was determined and considered to be a measure of the manganese dioxide present.

1 gram samples of the ores were placed in 250 ml Erlenmeyer flasks and 2 grams of Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) and 50 ml of 10 per cent sulfuric acid were added. The samples were digested on a hot plate until the black color in the flask disappeared. Small amounts of water had to be added to the flasks during the digestion due to evaporation. The samples were cooled and filtered. The excess Mohr's salt in the filtrate was titrated with a standard potassium permanganate solution. Blanks were treated the same as the samples to determine the permanganate equivalent of the Mohr's salt. The amount of manganese dioxide in each sample, calculated from the amount of available oxygen, is given in Table XII.

Table XII. Manganese Dioxide by Available Oxygen

Ore	Available O_2 (g./g.)	MnO_2 (g./g.)	Mn as MnO_2 (g./g.)	Mn in ore (g./g.)	Per cent of total Mn as MnO_2
Ark 1	0.05221	0.2835	0.1790	0.2355	76.00
Ark 2	0.07983	0.4330	0.2735	0.3190	85.65
Ark 3	0.06250	0.3395	0.2145	0.2977	72.13
Ark 4	0.06070	0.3299	0.2083	0.3160	66.00
Ark 5	0.05682	0.3083	0.1950	0.2700	72.22

Figure 2. Relation Between Amount of Manganese as Manganese Dioxide and Percentage Recovery

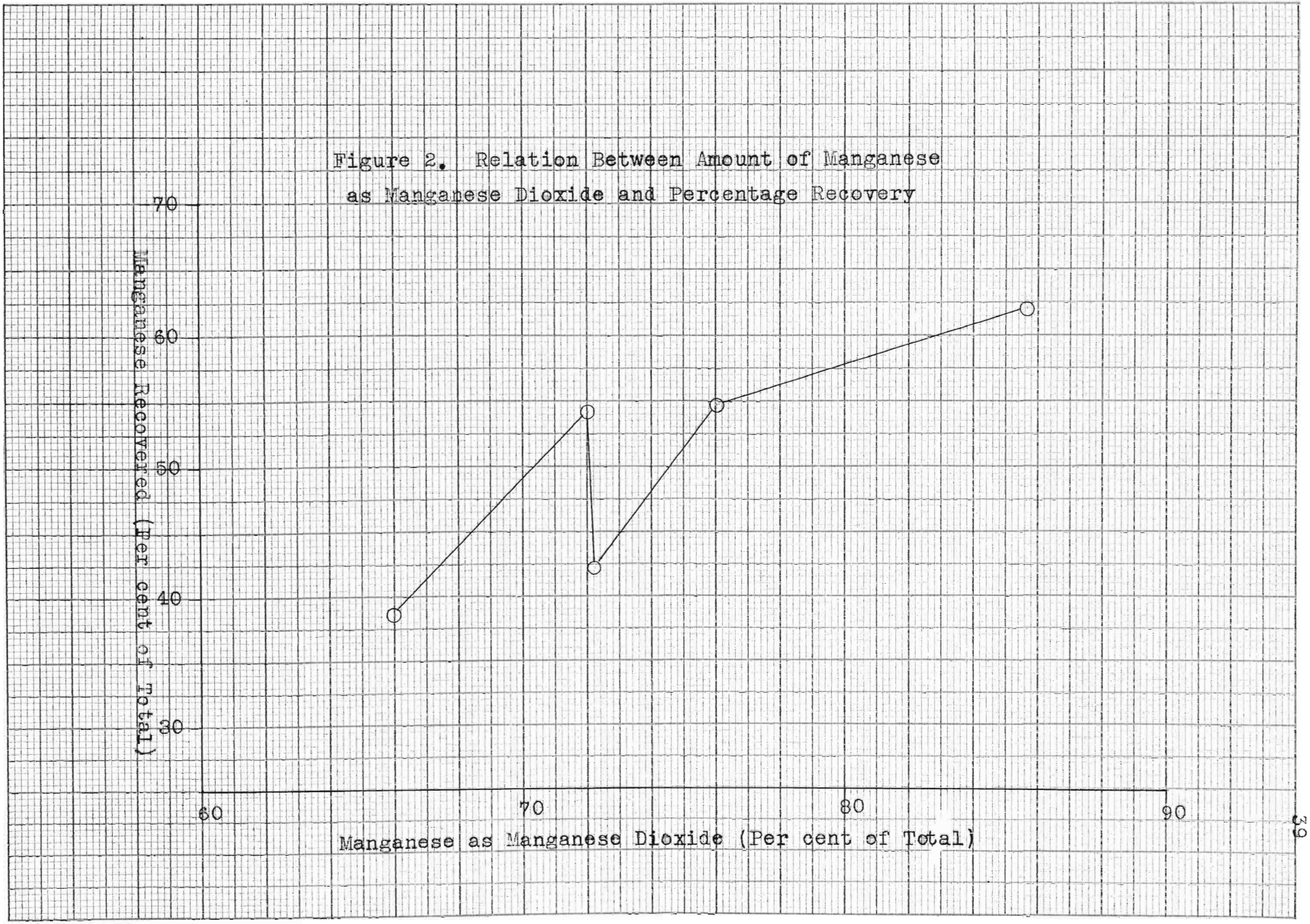


Figure 2 was obtained by plotting the percentage extraction data of Table IV (p. 22) against the percentage of manganese in the ore as manganese dioxide. This curve shows that there is a fairly direct relation between the manganese dioxide and the amount of extraction. The irregularity in the curve caused by Arkansas (5) ore was probably due to the greater density of this sample compared to the other samples. This density would cause less surface area of the ore to be exposed per unit weight. With this relation between the amount of extraction and percentage of manganese as manganese dioxide, the reaction involved in the sulfating of ores with sulfur dioxide could be represented by the equation:

$$MnO_2 + SO_2 \text{ — } MnSO_4$$

EFFICIENCY TESTS

A series of experiments was performed to determine the efficiency of extraction in leaching sulfated ores with water. Samples of Arkansas (1) ore were treated in the Burrell furnace with 5 per cent sulfur dioxide containing 1.7 per cent water vapor for 45 minutes at 650° C. After cooling, each sample was leached with a measured volume of water and the residue washed with a few ml of water. The soluble manganese in this leaching was determined. The residue was then leached with a large volume of water to remove the remaining soluble manganese and its amount determined. The manganese in the first leach divided by the total water soluble manganese gave the efficiency of extraction.

The results of these experiments, as shown in Table XIII, indicated that concentrations of manganese could be obtained that are high enough to make these solutions satisfactory for the production of electrolytic manganese. These solutions could also be used for the precipitation of manganese by several different methods.

Table XIII. Efficiency of Extraction

Exp. No.	Ore	Ml H_2O in first leach	Per cent total Mn in first leach	Amount of H_2O-soluble Mn (Per cent of total	Mn conc. in first leach(Per cent based on wt. water)	Efficiency
1	Ark 1	100	54.43	55.10	1.13	98.7
2	"	40	55.87	56.50	3.31	98.9
3	"	25	51.70	56.25	4.85	92.0
4	"	30	63.91	65.14	5.15	98.4

SUMMARY

1. The reaction between sulfur dioxide and minus 100-mesh ores was noticeably increased by introducing only 1.7 per cent water vapor in the sulfur dioxide.

2. 5 per cent sulfur dioxide containing 1.7 per cent water vapor gave a higher percentage recovery than did dry, 40 per cent sulfur dioxide.

3. The percentage recovery was increased by treating the ore while it was being heated and cooled.

4. Moistening the ore with very dilute solutions of sulfuric acid gave an increase in percentage recovery.

5. Leaching the treated ore with sulfuric acid gave recoveries as high as 80 per cent.

6. A solution containing as much as 5.15 per cent of manganese was obtained.

7. The manganous sulfate solution may be used for the recovery of manganese by many available methods.

8. The manganous sulfate solution obtained contained a higher concentration of manganous ion than is required in the electrolytic reduction of manganous sulfate.

9. The method used in these experiments is especially adaptable to Arkansas wad ores containing from 23 to 32 per cent manganese.

BIBLIOGRAPHY

Books

1. Hodman, C.D., and Holmes, H.N. Handbook of chemistry and physics. 25th ed. Cleveland, Chemical Rubber Publishing Co., 1941. p. 1449.

2. Lord, N.W., and Demorest, D.J. Metallurgical analysis. 5th ed. N.Y., McGraw-Hill, 1924. pp. 81-84.

3. Partington, J.R. Textbook of inorganic chemistry. 5th ed. N.Y., MacMillan, 1937. pp. 942-953.

4. Treadwell, F.P., and Hall, W.T. Analytical chemistry. 4th ed. N.Y., Wiley, 1915. Vol. II. pp. 624-625.

5. Willard, H.H., and Furman, N.H. Elementary quantitative analysis. 2nd ed. N.Y., Van Nostrand, 1935. p. 172.

Periodicals

1. Allen, R.C. Domestic manganese question. Min. & Met. Vol. 22, p. 177 (1941).

2. Betts, A.G. Exploiting our manganese resources. Iron Age. Vol. 147, pp. 56-59 (1941).

3. Dean, R.S. Electrolytic manganese and its potential metallurgical uses. Min. & Met. Vol. 22, pp. 5-8 (1941).

4. Dean, R.S. and others. Manganese metallurgy advances. Eng. & Min. J. Vol. 140, p. 42 (1939).

5. Finch, J.W. Adequacy of certain mineral resources. Mining Congress Journal. Vol. 27, No. 6, pp. 18-22.

6. Gaudin, A.M., and Behrens, R.H. Manganese recovery problem and its solution. Eng. & Min. J. Vol. 138, pp. 40-42 (1937).

7. Rousch, G.A. The present status of manganese. Military Engineer. Vol. 31, pp. 196-204 (1939).

8. Zapffe, Carl. Leaching manganese from the siliceous iron ores of Minnesota. Eng. & Min. J. Vol. 127, pp. 1039-1040, and Vol. 128, pp. 14-19 (1929).

U. S. Government Publications

1. Davis, C.W. Dissolution of various manganese minerals. U. S. Bureau of Mines. Report of investigations 3024. 1930. 11 pp.

2. Dean, R.S. Progress reports-metallurgical division. U. S. Bureau of Mines. Report of investigations 3600. 1941. 70 pp.

3. Dean, R.S., Leaver, E.S., and Joseph, T.L. Manganese; its occurrence, milling, and metallurgy. U. S. Bureau of Mines. Information circular 6770. 1934. pp. 165-191.

4. Knickerbocker, R.G., and Miller, Virgil. Smelting of manganese oxide, carbonate, or silicate ores with copper and iron sulfides. U. S. Bureau of Mines. Report of investigations 3659. 1942. 23 pp.

5. U. S. Bureau of Mines. Minerals yearbook, 1940. Manganese and manganiferous ores. pp. 567-584.

6. Van Barneveld, C.E. Leaching of manganese ores with sulfur dioxide. U. S. Bureau of Mines. Bulletin 173. 1920. pp. 57-64.

7. Woodman, F.W., and Jacobs, J.H. Studies in the electrodeposition of manganese. U. S. Bureau of Mines. Report of investigations 3681. 1943. 25 pp.

Patents

1. Bradley-Fitch Co. Leaching manganese ores. Brit. Pat. 319,605, June 19, 1928.

2. Bradley-Fitch Co. Recovering manganese from ores. Brit. Pat. 319,392, June 19, 1928.

3. Bradley, Wilson. Manganese recovery. U. S. Pat. 1,947,457. Feb. 20, 1934.

4. Brennan, J.H. Treating manganese ores. U. S. Pat. 1,768,112, June 24, 1930.

5. Dingmann, Theodore. Leaching manganese from ores. Ger. Pat. 687,016, Jan. 17, 1940.

6. Laury, N.A. Manganese value from ores. U. S. Pat. 1,761,133, June 3, 1930.

7. Leaver, E.S. Leaver drum-leaching process. U. S. Pat. 243,015, Nov. 18, 1918.

8. Sweet, A.T., and MacCarthy, J.D. Manganese extraction from ores. U. S. Pat. 1,962,160, June 12, 1934.

9. Sweet, A.T., and MacCarthy, J.D. Extracting manganese from ores. U. S. Pat. 2,176,774, and 2,176,775, Oct. 17, 1939.

10. Vander, C.S. Manganese recovery from ores. U. S. Pat. 1,807,642, June 2, 1931.

Unpublished Material

1. Pietz, Emil. Recovery of manganese from oxidized ores as iron-and phosphorous-free soluble salts. Thesis, Missouri School of Mines, Rolla, Missouri.

INDEX